

Exhaust Phosphorous Chemistry

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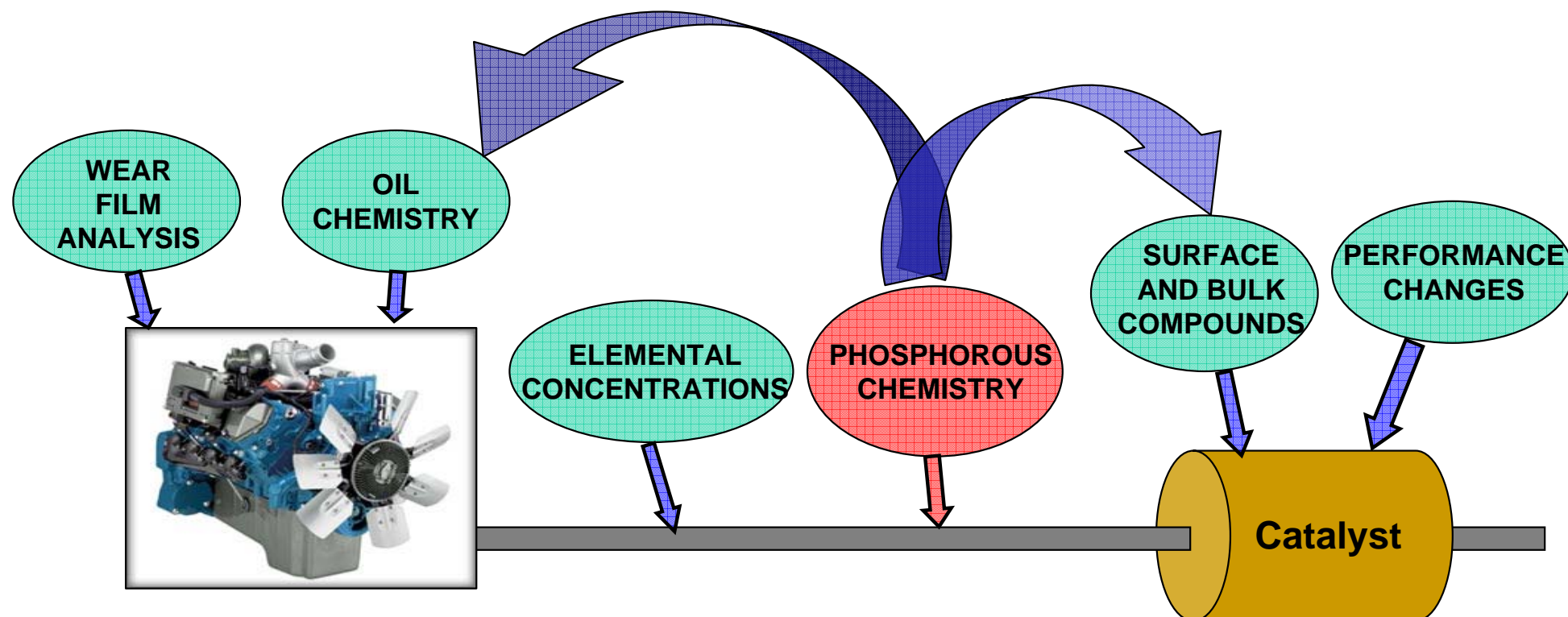
Phosphorous

- Zinc dialkyldithiophosphate (ZDDP) is used in lube oil
 - Contains zinc, sulfur, and phosphorous
 - Protects oxidation, corrosion, and wear protection
 - Various alcohols can be used to affect activity of ZDDP
- Phosphorous content in lube oil is being reduced
 - 1964 to 1989, no limit
 - 1994, 0.12% maximum
 - 1997 to 2002, 0.10% maximum
 - 2005, 0.08% maximum (proposed)
- Phosphorous is a well documented catalyst poison

Background

- Most phosphorous found in front 2" of catalyst
 - Affects light-off
- Phosphorous transfer to catalyst is typically high
- 2 to 16 grams of phosphorous per 120,000 miles typical for automotive
- Various ways have been used to study poisoning
 - Long mileage
 - Increased oil consumption
 - Doped fuel
 - Doped lube oil
 - Doped exhaust
 - Direct impregnation
- Phosphorous chemistry is complex and depends on method of introduction and other materials present

Lube oil additive related measurements



Can exhaust phosphorous chemistry measurements provide a link between additive chemistry and catalyst reactions?

Exhaust Phosphorous Chemistry

**LUBE OIL
+ ENGINE**

**EXHAUST
CHEMISTRY**

CATALYST

ZDDP

ZDDP –

ZnPO₄

P₂O₅

Ca

Mg

Mn

Other phosphates

NO_x

Nitrates

SO₃

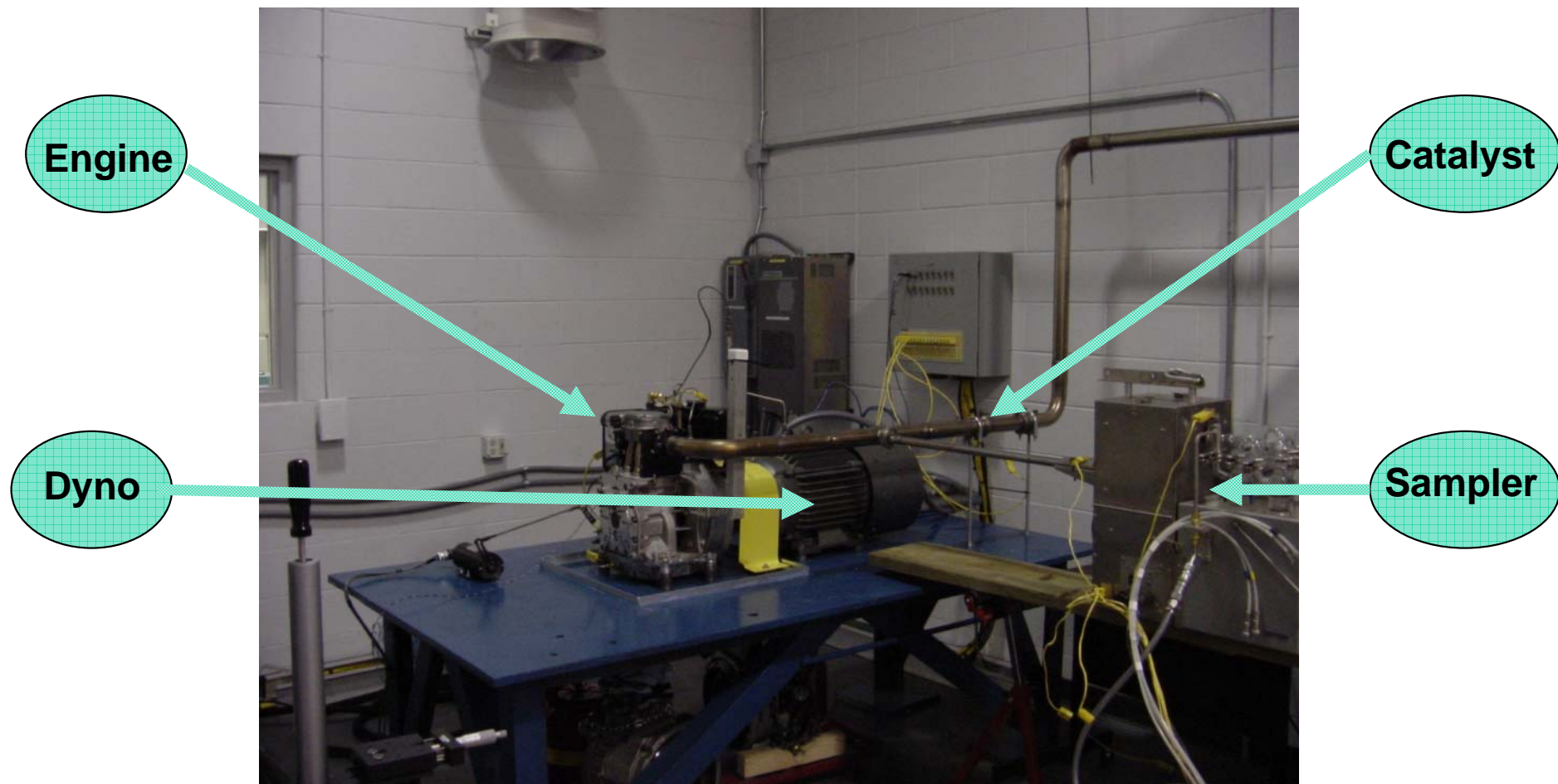
Sulfates

**GLASSY
COATINGS**

**FLUFFY
COATINGS**

**BULK
WASHCOAT
COMPOUNDS**

Experimental set-up



Catalyst and holder



Sources of materials

- Engine
 - Hatz
 - 500 cc single cylinder DI diesel
- ZDDP additives
 - Elco Corporation
 - 4,5,8 primary alcohols
 - 2 secondary alcohols
- Catalyst substrates
 - NGK
 - Cordierite, 200 cpsi, 12 mil, 2" dia x 3" long
- Model catalysts
 - Engelhard Corporation
 - Diesel oxidation catalyst (low PM, alumina, ceria)
 - Diesel NOX adsorber catalyst (Pt, barium, alumina)

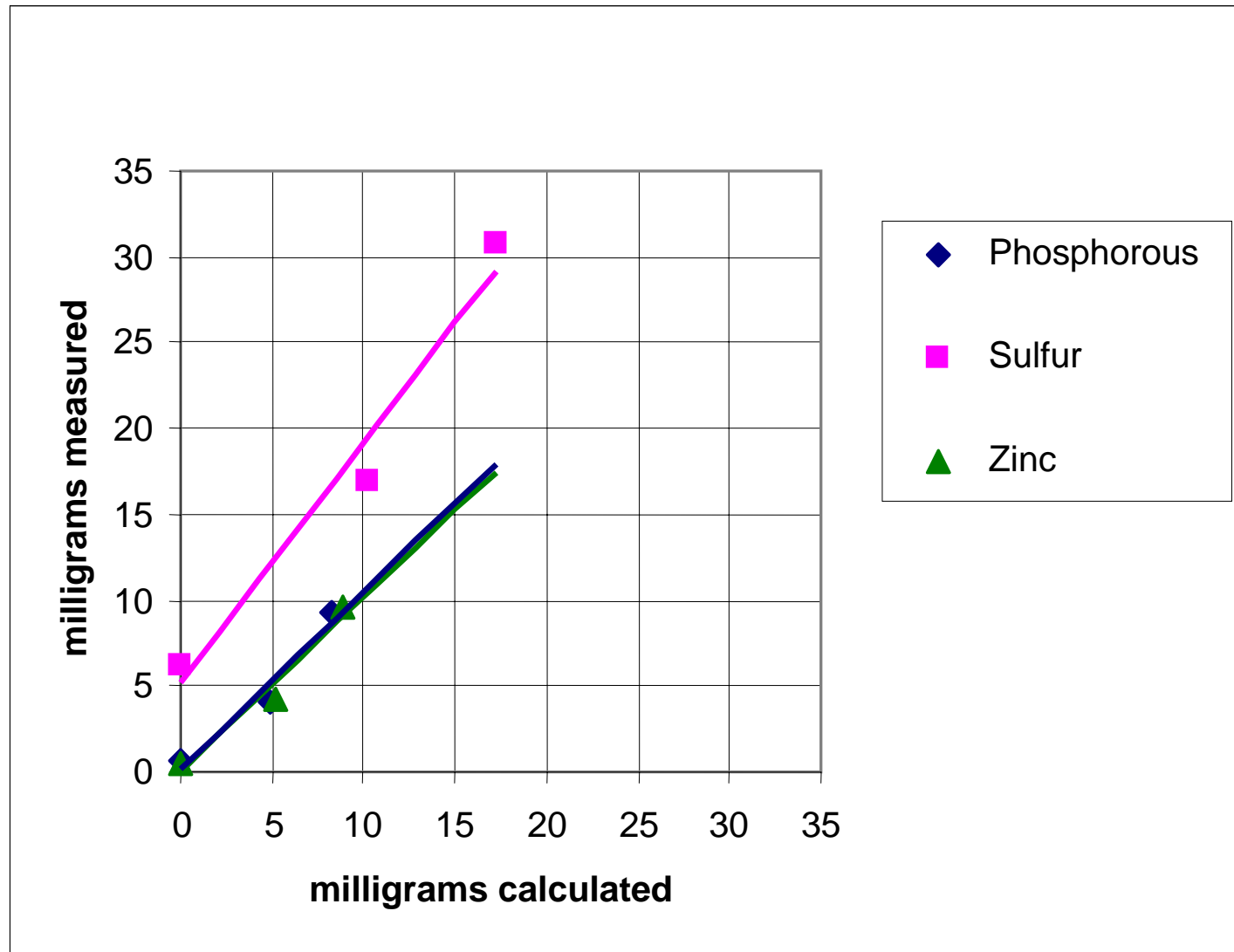
Sampling and analysis – part 1

- Measurement capability development
 - Dope ZDDP into fuel
 - Vary engine load to vary exhaust temperature
 - Hot exhaust sampling

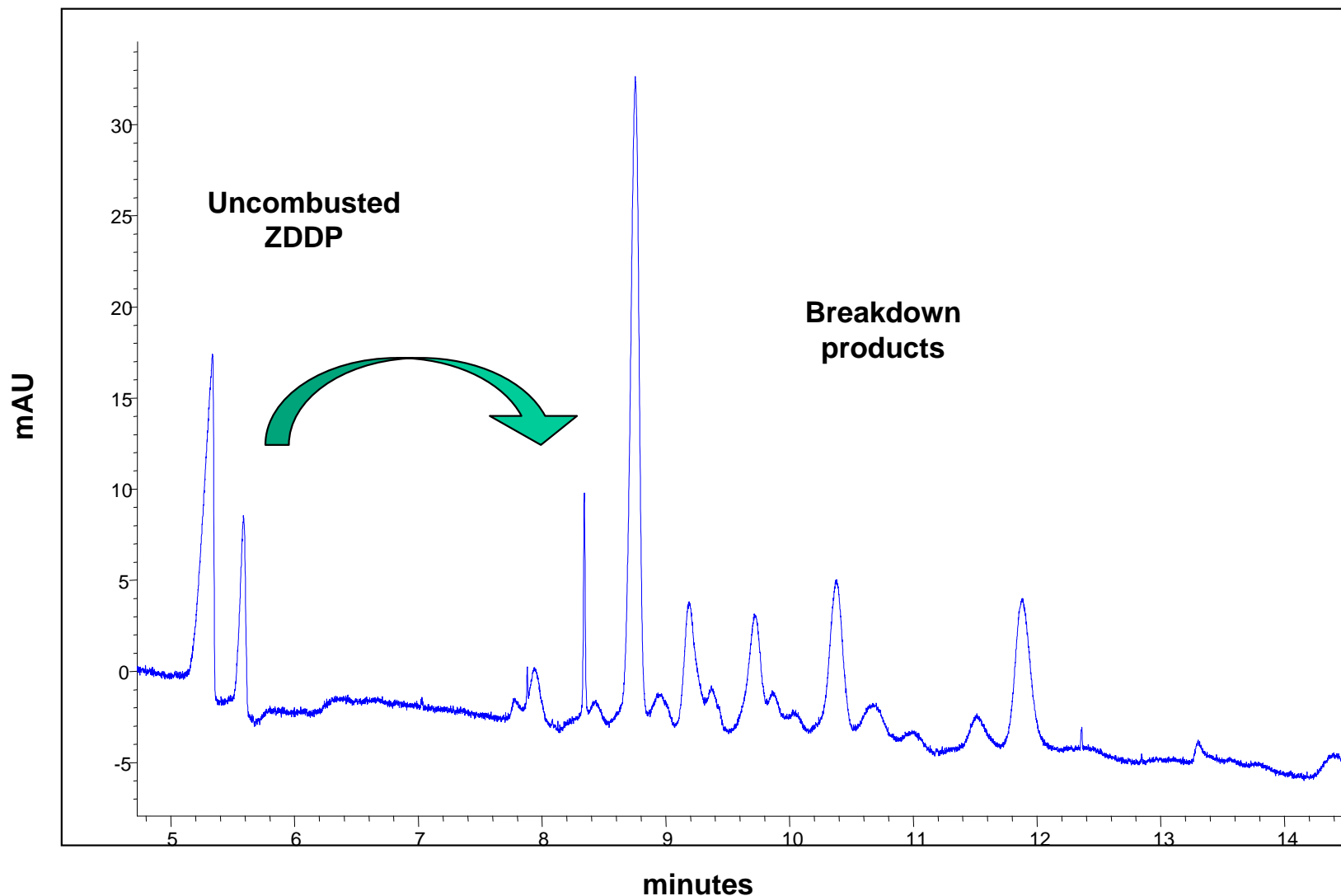
Phase 1 – measurement development

- Metals analysis
 - Filters and impingers
 - XRF and ICP
- Compound identification
 - Filters and impingers
 - FTIR
 - GC-MS
 - Electrospray MS
 - Capillary-electrophoresis
 - Raman
- Catalyst analysis
 - Raman
 - DRIFTS

Elemental balances



CE electropherogram – ZDDP in engine exhaust 230 nm UV adsorption



Sampling and analysis – part 2

- How do engine / lube oil changes affect exhaust chemistry?
 - Dopant formulation
 - Presence of other metals
 - Path for introduction
- How do exhaust chemistry changes affect catalyst?
 - Surface compounds
 - Bulk reactions
 - Catalytic activity

Project status

- Literature review and discussions
- Engine set up and running
- Sampling and methods development underway
- Identification of ZDDP breakdown products underway